TREATMENT FOR WASTE PICKLING SOLUTIONS CONTAINING IRON AND METHOD OF FERRIC OXIDE FORMATION

BACKGROUND OF THE INVENTION

1) FIELD OF THE INVENTION

The present invention relates to the recovery of solutions utilized for industrial cleaning and processing as well as the extraction of ferric oxide suspended therein, specifically, a treatment for waste pickling solutions containing iron and method of ferric oxide formation.

2) DESCRIPTION OF THE PRIOR ART

In the metal finishing industry, pickling process is a commonplace process. As for its theoretical basis, a pickling normally consists of a hydrochloric acid (HCl) solution that scales steel and iron surfaces, the remnants of which end up as ferric oxide, and thereby enables the further finishing of the said ferrous materials. As such, the chemical reaction based on the pickling principle is as follows:

Ferric Oxide from the Pickling of Surfaces

$$\begin{matrix} & FeO & & \\ Fe + & Fe_2O_3 + HCl & \longrightarrow & FeCl_3 + H_2O \\ & Fe_3O4 \quad H_2O & & FeCl_2 \end{matrix}$$

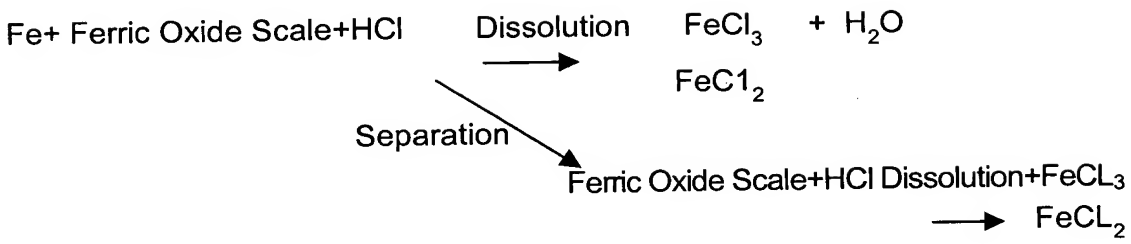
Ferrous Material: Scale

Ferrous Material Pickling Reaction

$$\begin{matrix} Fe + HCl & \longrightarrow & FeCl_2 + H_2\uparrow \\ H_2O & & \end{matrix}$$

Additionally, the mechanism of the acid during ferric oxide scaling after the adding of the hydrochloric acid results in the following reaction:

Pickling Mechanism



At the same time, the pickling efficiency, as well-known, is characterized by an increase in iron content after the onset of the acid wash followed by a corresponding reduction in acid washing efficiency, as shown in the example below:

Fe+Ferric Oxide Scale+HCl (15%) $FeCl_3$ (40-60g/L) ⟶	HCl (6-10%) (Reduced) $FeCl_3$ (80-100g/L) (Raised)
Ferrous Deterioration 0.2-0.8%	Fe content higher, efficiency reduced.

As a result, the hydrochloride concentration gradually decreases and the iron ion concentration gradually increases during the treatment process such that after a certain period, acid washing efficiency is reduced until all effectiveness is lost and the solution must be replaced. In simple terms, the spent acid solution still contains six to 10 percent HCl, a highly corrosive substance that is subject to controls, utilized for industrial processes, and now among the most serious pollutants in the world.

Acid processing methods in current steel and iron industries can be listed in several types below and, furthermore, each has its advantages and disadvantages:

(1) Ruthner Method: This process is a spray roasting approach capable of recovering hydrochloric acid and Fe_2O_3. Its advantages are low pollution, total resource recovery, and a sufficiently high level of technology, with the disadvantages including considerable capital investment, high operating cost, and difficult maintenance. As such, only large-scale steel and iron manufacturers have the capacity to utilize this method.

(2) Keram, Chernie GMBH Method: This is basically a flowing bed-type thermal oxidation process capable of recovering HCl and ferric oxide. It generally shares the same advantages as the Ruthner method, but since recovered ferric oxide quality and quantity is poor, only large plants have the requisite capability.

(3) Chlorination Method (or Distillation Method): Consists of a concentrated chlorinating solution process to obtain $FeCl_3(aq)$, $FeCl_3+6H_2O(s)$, and other by-products. The advantages are moderate investment, equipment, and operating costs, with the disadvantages including serious air pollution to the extent that marketing the derived by-products is difficult.

(4) Waste Water Treatment Method: This is a neutralizing, agglutinating, and precipitating approach to obtain large volumes of $Fe(OH)_2$ from hazardous sludge and, furthermore, does not involve any resources and is the method often utilized by medium- and small-size factories.

(5) Transport and Discard Method: This is the most inefficient method and since it consists of unlawfully dumped refuse that results in environmental pollution, the approach is prohibited.

(6) Sulfuric Acid Displacement Method: A process consisting of displacing HCl in spent acid with sulfuric acid to produce ferrous sulphate. Now in the research stage, its commerical product viability has not been established, but product direction is limited and purity is questionable.

In addition to the advantages and disadvantages of the said methods,

each method essentially involves the storage of the spent acid in separate containers or tanks, where the treatment process is then performed, and treatment cannot be undertaken at the production line. As a result, manufacturers are required to have remote acid solution tanks for treatment alone that must be replenished and cleaned every three to seven days, a routine that is troublesome and dangerous.

In view of the said situation, the applicant conducted extensive research and experimentation based on years of experience gained while engaged in the fields of environmental protection and resource recycling to overcome the drawbacks of said methods that culminated in the successful development of the treatment for waste pickling solutions containing iron and method of ferric oxide formation of the present invention which provides for a treatment method at the production line capable of maintaining the optimal acidity and iron concentration of acid wash tank solutions as well as a ensuring total resource utilization.

To enable a further understanding of the general technological content of the present invention, the brief description of the drawings below are followed by the detailed description of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention can be more fully understood by reference to the following detailed description and accompanying drawings, in which:

Figure 1 is a flowchart of the present invention; and

Figure 2 is a diagram of the treatment installation of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

As shown in the Figures 1, the treatment method of the present invention consists of processing the pickling solution from a production line situated pickling tank, which is collectively recovered or directly taken from the pickling tank and

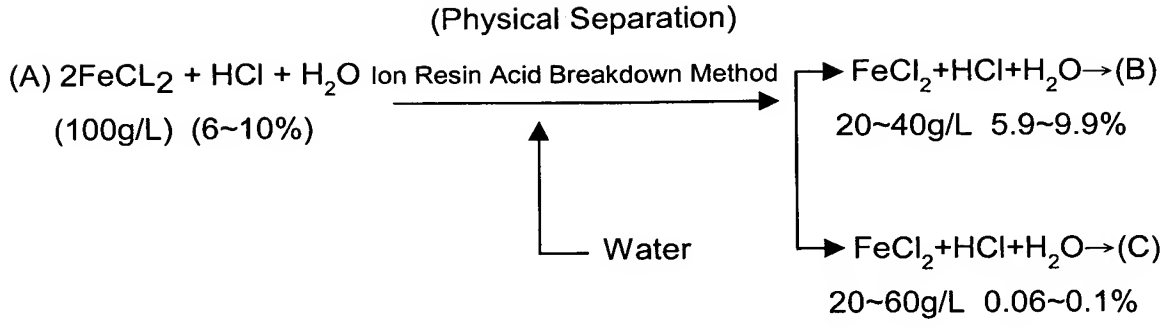
later undergoes a photochemically induced oxidation reaction procedure and a magnetic culling procedure to complete.

As indicated in Figure 2, the spent acid of the present invention in the disposaled waste acid tank **A** is admitted into the acid recovery equipment **B**, the said acid recovery equipment **B** desalts the pickling tank with industrial-use water **C** to facilitate recovery, and the liquid now having a high iron content and low acidity is forwarded into a mixing tank **D**, and sodium hydroxide is added into the mixing tank **D** to adjust the pH value, following which the liquid is run through a filter **E**, the said filter **E** being a bag-type screening medium; however, the procedure is not limited to this.

Following filtration, the spent acid that had been left acid and added into the sodium hydroxide enters a photo-oxidation reaction device **F**. The photo-oxidation reaction device is a tank basically; therefore, the sodium hydroxide and the air can be added depends on the requirement. Meanwhile, the liquid has a circular loop, namely an ultraviolet beam circuit **G**, and the ultraviolet beam circuit **G** irradiates with proper wavelength. As shown in Figure 2, in order to react completely, a stirring device is equipped inside the mixing tank **D** and the photo-oxidation reaction device **F** for stirring.

Referring to the drawings, since iron particles are disassociated after the photo-oxidation of the liquid, a magnetic culling procedure is executed for further solids separation such that the iron particulate still suspended as solids in the liquid are separated by magnetic attraction as ferric oxide particles and, furthermore, overflowing water utilized is only released after undergoing a desalting process to avert environmental pollution problems.

To demonstrate that the present invention is workable, the applicant provides the following chemical reactions as evidence.



(B) ⟶ Recovered acid to pickling tank (thus, production line usable)

(C) ⟶ $FeCl_2$+HCL+H_2O Magnetic Reaction ⟶

20~60g/L .06~0.1%

NaOH and $\frac{1}{2}O_2$

$HCl + NaOH \longrightarrow NaCl + H_2O$ (Photo-Oxidation Reaction)

$FeCl_2 + NaOH \longrightarrow Fe(OH)_2 + 2\,NaCl$ Magnetic Reaction (D)

$2\,Fe(OH)_2 + \frac{1}{2}O_2 \longrightarrow Fe_2O_3 + 2\,H_2O$ (D)

(D) ⟶ Separation of suspended solids from solution (magnetic selector) ⟶

Filtered ferric oxide particles (E)

(E) ⟶ H_2O + NaCl (aq) ⟶ EP-compliant waste water discharge (F)

⟶ Fe_2O_3 Spray Dried ⟶ γ -Fe_2O_3(S) By-product (G)

300℃ Blast

The ferric oxide derivation achievable by the embodiment of the present invention is comparable to that of the Ruthner method, with the chemical analysis shown in the following table:

wt%	Fe_2O_3	SiO_2	Cl^-	Surface Area
Ruthner	98.0-99.8	0.05-1.0	0.08-0.09	1.7-8.0
Present Invention	98.0-99.0	0.08-0.09	0.02-0.05	0.65-0.93

As is well-known, Fe_2O_3 can be utilized as magnetic material that is of higher value than iron itself and, thus enhances its added value as well as effectively solves spent acid treatment problems, especially wet-type, normal temperature treatment, in which the high added-value ferric oxide also affords an ingredient that is totally free of secondary pollution, has a low economy of scale, and involves a facilities cost that is less than that of the Ruthner method widely utilized by large factories and, furthermore, since it is capable of treatment at the production line and controlling the ferrous density of acid solutions in the pickling tank to the most optimal concentration such that productivity is increased, the treatment and method of the present invention is a breakthrough in this field.

The disclosure of the present invention is but one most preferred embodiment and all modification and embellishments based on the technical concepts of the present invention by persons skilled in the technology shall not remain protected by the patented scope and claims of the present invention.

In summation of the foregoing section, since the present invention possess technological features differing from that of the prior art, the present invention meets patent application requirements and is submitted to the examination committee for review and the granting of the commensurate patent rights.